(19) [Issuing Country] Patent Office of Japan
(12) [Gazette Type] Official Gazette for Unexamined Patents
(11) [Disclosure Number] Hei-11-139815
(43) [Date of Disclosure]
(54) [Title of Invention] Carbon nanotube device and its manufacture
(51) [International Patent Classification Vol. 6]
C01B 31/02 101
B01J 23/86
23/89
D01F 9/127
H01B 1/04
[F1]

C01B 31/02	101Z
B01J 23/867	M
23/89	M
D01F 9/127	
H01B 1/04	

[Request for Examination] Not requested
[Number of Claims] 6
[Mode of Application] OL
[Number of Pages] 11
(21) [Application Number] Application No. 9-305512
(22) [Filing Date] November 7, 1997
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(57) [Summary]

[Problem To Be Solved] To provide a carbon nanotube device which is capable of efficiently allowing current to flow through the carbon nanotubes by joining one end or both ends of each of carbon nanotubes to the electrode on a substrate provided with an electrode and further, capable of controlling the amount of current flowing through the carbon nanotubes with a magnetic field. [Solution] The manufacture comprises heating a substrate that has a surface layer in which catalyst hyperfine particles each containing Fe, Co or Ni are dispersed in a material consisting essentially of Cu, Ag, Au or Cr, to 400 to 800∘C in an atmosphere containing ethylene, acetylene or gaseous carbon monoxide as a gaseous raw material, to subject the gaseous raw materials to thermal decomposition and thereby to grow carbon nanotubes on the surface of the substrate.

Scope of Patent Claim

[Claim 1] A carbon nanotube device in which at least one end of said carbon nanotubes is connected to a substrate, and catalyst hyperfine particles containing one or more metals selected from Fe, Co or Ni are dispersed at the junction in material consisting essentially of one or more metals selected from Cu, Ag, Au or Cr.

[Claim 2] The carbon nanotube device of Claim 1 in which aforementioned substrate is Si, aforementioned catalyst hyperfine particles contain one or more metals selected from Fe or Co, and that is dispersed in material consisting essentially of Cu.

[Claim 3] The carbon nanotube device of Claims 1 or 2 in which the current flowing through aforementioned carbon nanotubes is modulated by an external magnetic field.

[Claim 4] A method of producing carbon nanotube devices in which carbon nanotubes are grown by thermal decomposition using a catalyst on a substrate, wherein carbon nanotubes are grown from the surface of a substrate comprising catalyst hyperfine particles containing one or more metals selected from Fe, Co or Ni that are dispersed in material consisting essentially of one or more metals selected from Cu, Ag, Au or Cr, at which time the substrate with said section of dispersed catalyst hyperfine particles is heated in an atmosphere of ethylene, acetylene, gaseous carbon monoxide or a mixture thereof as a gaseous raw material at a temperature range of 400 to 800∘C to bring about a thermal decomposition reaction of said gaseous raw material.

[Claim 5] A method of manufacturing the carbon nanotube device pursuant to Claim 4 in which aforementioned substrate is Si, aforementioned catalyst hyperfine particles contain one or more metals selected from Fe or Co, and that is dispersed in material consisting essentially of Cu.
[Claim 6] The method of manufacturing the carbon nanotube device pursuant to Claims 4 or 5 in which the current flowing through aforementioned carbon nanotubes is modulated by an external magnetic field.

Detailed Description of the Invention
[0001]

[Technical Field of Invention] The present invention concerns carbon nanotubes which are effective as functional devices such as quantum effect devices, electronic devices, micromachining devices, bio devices, and their manufacture. In particular, it concerns carbon nanotubes that are ideal for electronic devices in which the amount of current flowing through is controlled by a magnetic field as well as their manufacture.

[0002]
[Related Art] Fibrous carbon is generally known as carbon nanotubes, and numerous methods of producing thick carbon fibers having diameter of several μm or more used as structural material have been researched. The principal methods of production at present use pitch or PAN raw material. A brief outline of the production method indicates that raw material spun from PAN fibers, isotropic pitch or mesophase pitch is rendered infusible and flame-proof, carbonized at 800 to 1400°C, and then subjected to high-speed processing at 1500 to 3000•C. The resulting carbon fibers are used as composite constituents of structural material in automobile development, aerospace-related applications, thermal insulation and sports gear because of their outstanding mechanical characteristics, including strength and modulus of elasticity, and because of their light weight.

[0003] Carbon nanotubes that have appeared in recent years are tubes whose diameter is under 1 μm. Tubes having hexagonal carbon lattice planes parallel to the tube axis are ideally formed, and such tubes could be multiplied. Such carbon nanotubes would theoretically be expected to function as metals or semiconductors based on the method of connecting hexagonal lattices of carbon and on the tube thickness, and are expected to serve as future functional material. Arc discharge is commonly used in the synthesis of carbon nanotubes, but research has been carried out in recent years on laser evaporation, thermal decomposition and plasma utilization.

[0004] The conventional technique for carbon nanotubes is briefly summarized below.

[0005] There are numerous types of carbon fibers available, and the method of synthesis must be selected based on the application. The structure of the synthesized fibers is known to vary greatly depending on the method of synthesis and the synthesis conditions. The details are stated in "New Carbon Material" (Gijutsudo Shuppan) by Michio Uegaki. The three main types of synthesis are briefly explained below.

[0006] 1) PAN-based carbon fiber raw material is synthesized via the three main processes of spinning a precursor using polyacrylonitrile, infusible processing and high-temperature processing. Cyclization and dehydrogenation by oxygen followed by dehydrocarbonization in formation of hexagonal carbon lattices are the steps followed in infusible processing and in high-temperature processing. Hexagonal carbon lattices are oriented in the fiber axial direction by adding a fiber-stretching step in the process, and the characteristics are known to be enhanced markedly. The resulting PAN-based carbon fibers come in general purpose (GP) grade and in high tensile strength (HT) type.

[0007] 2) Pitch carbon fibers are classified into two primary types of isotropic pitch carbon fibers produced from isotropic pitch and mesophase pitch carbon fibers that exhibit optical anisotropy. The production process comprises carbonization by infusible processing and high-temperature processing similar to aforementioned PAN carbon fibers.

[0008] Mesophase pitch carbon fibers have good axial orientation even without stretching as in PAN-based carbon fibers, and the structure of the fiber cross sections, including radial, random, or coaxial tubes (onions) can be controlled by the viscosity of the pitch. Mesophase pitch carbon fibers are the high modulus (HM) type that have attracted attention as future composite material. Isotropic pitch carbon fibers are the GP grade utilized in such applications as thermal insulation.

[0009] 3) One representative example of gaseous phase grown carbon fibers is the method in which benzene vapors are fed with hydrogen carrier gas into an electric oven held at about 1050•C, followed by growth on a substrate using fine iron particles as the catalyst. There are three growth phases in the course of growth; nucleus formation, growth in the axial direction of extremely fine fibers, and growth in the fiber radial direction to increase fiber thickness. Hyperfine particles on the order of 10 nm are required in the catalyst, and Fe_3C is found at the tip of fibers that are obtained. They are believed to inhibit iron reduction and benzene decomposition in hydrogen gas. The resulting fibers comprise hollow tubes from the core, with flat, thin reticular layers and a 1-mm thick reticular outer periphery axially arrayed virtually in parallel. Since hollow tubes with flat, thin reticular layers near the core have an iron catalyst forming the nucleus, the thick outer periphery is concluded to be formed by thermal decomposition of benzene. Such tubes are also seen in gaseous phase thermal decomposition of carbon monoxide using iron as the catalyst. G.G.Tibbetts, in J.Cryst.Growth, 73 (1985) 431, has explained that fibers are similarly obtained using methane gas.

[0010] There are two types of gaseous phase growth; the seeding catalyst method in which a catalyst is attached to a substrate, and the floating catalyst method in which a catalyst is floated in a gas. Fibers grown in the floating catalyst method have a fine diameter and are prone to bending. Furthermore, Ishioka et al. explained in Carbon, 30 (1992) 859 and Carbon, 30 (1992) 865, that the fiber yield could be enhanced by using hydrogen and mixed gas of carbon monoxide/carbon dioxide as the carrier gas, and that the fiber yield could be enhanced still more by using a mixture of ferrocene and metal acetylacetonate as the catalyst.

[0011] A graphite-like laminated structure is reached by adding heat-treatment to fibers obtained in the seeding method. Specifically, a reticular structure is reached near 2000•C, and a laminated reticular structure is reached from the vicinity of 2500•C. A laminated graphic structure is not developed in fibers produced by the floating catalyst method. Polygonization develops in which the fiber outer layer forms polyhedrons upon heat treatment of these fibers at temperatures of

2800 ◦ C or more.

[0012] Overall examination of these production methods reveals that the PAN, pitch systems require flame-proofing, infusible processing in the range of 150 to 400 ◦ C in air, followed by carbonization, graphitization heat treatment, which is also required in the gaseous phase growth method. Specifically, there are carbonaceous materials that are carbonized by heat treatment near 1300 ◦ C as well as graphite materials that are graphitized near 2800 ◦ C. There is a tendency for the density to increase and for the resistance to decrease accompanying such heat treatment. Examination by material type reveals that the density, tensile strength and tensile elasticity increase while the resistance falls in sequence of isotropic pitch, PAN, mesophase pitch and gaseous phase growth. A turbostratic structure persists even after high-temperature heat treatment of isotropic carbon fibers having mean spacing of 0.344 nm. However, an ideal laminated structure is obtained with mean spacing of 0.336 nm following high-temperature heat treatment above 2400 ◦ C in gaseous phase grown carbon fibers. This could also be evaluated from measurement of the magnetic resistance.

[0013] The diameter of carbon fibers obtained in the production method stated above exceeded several μm, but comparison of these revealed that the gaseous phase growth method most readily produced material approaching carbon nanotubes with a laminated reticular structure parallel to the axis and a narrow diameter.

[0014] Conventional carbon nanotube techniques that have been developed in recent years are explained here.

[0015] Material whose diameter is finer than that of carbon fiber and under 1 μm is differentiated between carbon nanotubes and carbon fibers, but there is no specific boundary. In this specification, the decision was made to denote slender material whose diameter exceeds several μm as carbon fibers and slender material whose diameter is under 1 μm as carbon nanotubes. In a narrow sense, the term carbon nanotubes denotes material in which hexagonal carbon lattice planes are virtually parallel to the axis, and it includes the case in which amorphous carbon is present about the periphery of carbon nanotubes.

[0016] Carbon nanotubes are further classified as single wall nanotubes (abbreviated SWNT), in which hexagonal reticular tubes have a single-layer structure, and multi-wall nanotubes (abbreviated MWNT) having a multi-layer hexagonal reticular tubular structure. The structure of carbon nanotubes that are obtained is determined to a certain extent by the synthesis method and conditions, but the creation of carbon nanotubes having a given structure has not been possible.

[0017] The structures of these carbon nanotubes are briefly summarized in Figure 1. Figure 1 a) to d) shows, on the left, a general view of a carbon nanotube from the side while the right shows a cutaway drawing. Carbon fibers have a shape like that shown in Figure 1 a) in which the diameter is large but a cylindrical reticular structure parallel to the axis is not developed. A tubular reticular structure parallel to the axis near the tube core as shown in Figure 1 b) is developed by the gaseous phase thermal decomposition method applying a catalyst, but carbon having a scattered structure is often attached about the periphery. MWNT, a reticular tubular structure parallel to the axis with a reduced amount of amorphous carbon about the periphery, as shown in Figure 1 c), is formed by arc discharge. Furthermore, a tubular reticular structure lacking multiple layers as shown in Figure 1 d), so-called SWNT, is reached by the arc discharge method and laser vapor deposition.

[0018] At present, there are three main methods of producing aforementioned carbon nanotubes. They are the carbon-fiber gaseous phase growth method and similar methods, the arc discharge method and the laser vapor deposition method. Additional methods include the plasma synthesis method and the solid-phase reaction method. These three typical types are briefly explained below.

[0019] 1) Thermal decomposition method using a catalyst. This method is virtually identical with the carbon fiber gaseous phase growth method. This production method was stated in International Patent Application, Publication Number WO89/07163, by C.E. Snyder et al. Ethylene and propane are introduced with hydrogen into a reaction vessel, and metal hyperfine particles are inducted concurrently. Other permissible gaseous raw materials include saturated hydrocarbons such as methane, ethane, propane, butane, hexane, cyclohexane; unsaturated hydrocarbons such as ethylene, propylene, benzene, toluene; as well as acetone, methanol or oxygen in such forms as carbon monoxide. A desirable ratio of gaseous raw material to hydrogen would be in the range of 1:20 to 20:1, with recommended catalysts including Fe or mixtures of Fe with Mo, Cr, Ce, Mn. The method of adhering this to fumed alumina is also advocated. A reaction temperature in the range of 550 to 850∘C, a gas flow rate of 1000 sccm of hydrogen per inch diameter and 200 sccm of gaseous raw material containing carbon would be desirable. Fine particles are induced and carbon nanotubes are grown in 30 minutes to one hour.

[0020] The shape of carbon nanotubes obtained in this manner would be diameter of 3.5 to 75 nm and length of 5 to 1000 times the diameter. The carbon reticular structure would be parallel to the tube axis and adhesion of thermal decomposed carbon to the outside of the tube would be slight.

[0021] H. Dai et al. has reported in Chemical Physics Letters 260 (1996) pp. 471-474 that SWNT is created by reaction at 120∘C using carbon monoxide as the gaseous raw material and Mo, metal with poor growth efficiency, as the catalytic nucleus.

[0022] 2) Arc discharge method. The arc discharge method was first discovered by Iijima et al., who presented the details in Nature Vol. 354 (1991), pp. 56-58. The arc discharge method is a simple method in which direct-current arc discharge is carried out using carbon rod electrodes in an argon atmosphere of about 100 Torr. They are grown along with fine carbon particles of 5 to 20 nm on the surface of the cathode. Such carbon nanotubes are 4 to 30 nm in diameter, about 1 μm long, and have a layered structure of 2 to 50 overlapping tubular carbon lattices. The reticular carbon structure forms a spiral parallel to the axis. The spiral pitch varies among tubes or within each layer of a given tube, and the layer separation in a multi-layered tube would be 0.34 nm, which virtually coincides with the layer separation of graphite. The tube tips are closed in a carbon network.

[0023] T.W.Ebbesen et al. have stated the conditions for creating large amounts of carbon nanotubes by the arc discharge method in Nature Vol. 358 (1992) pp. 220-222. Carbon rods of 9 mm diameter for the cathode and of 6 mm for the anode were set on opposite sides of a chamber at a 1 mm separation. Arc discharge of about 18V, 100A was generated in an atmosphere of about 500 Torr helium. The proportion of carbon nanotubes was slight below 500 Torr while the overall amount that was created decreased above 500 Torr. At 500 Torr, the ideal condition, the proportion of carbon nanotubes in the product reached 75%. The yield of carbon nanotubes declined if the applied power were altered or the atmosphere was switched to argon. Furthermore, many nanotubes formed near the core of the carbon rods that were created.

[0024] 3) Laser vapor deposition. Laser vapor deposition was reported by T. Guo et al. in Chemical Physical Letters 243 (1995) pp 49-54, and the creation of rod-shaped SWNT by laser vapor deposition was reported by A. Thess et al. in Science Vol. 273 (1996) pp. 483-487. This method is outlined below. First, a carbon rod in which is dispersed Co or Ni is disposed in a quartz tube which is then filled with about 500 Torr of Ar, followed by heating to 120•C. An NdYAG laser is then focused on the upstream side of the quartz tube from the tip to heat the carbon rod and evaporate it. Carbon nanotubes then collect on the downstream side of the quartz tube by so doing. This method is a promising method of selectively creating SWNT, and is characterized by the ease of SWNT collection and rod formation.

[0025] A conventional technique of applying carbon nanotubes is explained next.

[0026] No products that apply carbon nanotubes are available at present, but research directed toward their practical application is actively underway. A typical example thereof is briefly explained below.

[0027] 1) There are many examples of research in which carbon nanotubes are used as electron sources because their tips are sharp and they are electrical conductors. In Science Vol. 270 (1995) p. 1179, W.A. de Heer et al. passed carbon nanotubes obtained via arc discharge through a filter in refining and erected them on a substrate as an electron source. The electron source in this report was a collection of carbon nanotubes, but discharge current exceeding 100 mA could be stably collected by applying 700 V from an area of 1 cm^2. In addition, in Science Vol. 269 (1995) p. 1550, A.G. Rinzler et al. attached one carbon nanotube obtained through the arc discharge method to an electrode and evaluated its characteristics. The results showed that the application of about 75 V voltage produced about 1 nA of discharge current from a carbon nanotube with a sealed tip and about 0.5 μA from a carbon nanotube with an open tip.

[0028] 2) STM, AFM. H. Dai et al. reported on the application of carbon-nanotube STM, AFM in Nature 384 (1996) p. 147. Carbon nanotubes are created by the arc discharge method. The tip forms a SWNT of about 5 nm diameter. Even the bottom between gaps in the sample can be observed since the tip is narrow and supple, and that produces an ideal tip that does not crash.

[0029] 3) Hydrogen storage material. A.C. Dillon et al. reported in Nature Vol. 386 (1997) pp. 377-379 that multiples of hydrogen molecules could be stored by using SWNT compared to carbon that is produced from pitch raw material. Furthermore, examinations involving applications have just begun, but it is expected to serve as hydrogen storage material for use in future hydrogen-powered automobiles.

[0030]
[Problems Solved by the Invention] The structure as well as the thickness and orientation of carbon nanotubes produced using conventional technology are quite random, and electrodes are not joined to carbon nanotubes immediately after growth. Specifically, carbon nanotubes are recovered and refined following synthesis, and they must be formed to specific shapes in conjunction with their mode of use. For example, one carbon fiber is isolated for use as an electron source, and an electrode must be bonded on one side, as shown by A.G. Rinzler et al. in Science Vol. 269 (1995) pp. 1550-1553. Furthermore, carbon nanotubes produced by arc discharge must follow a course of refining, followed by erecting the tubes on a substrate using ceramic filters, as shown by Walt. A. de Heer et al. in Science Vol. 270 (1995) p. 1179-1180 and Science Vol. 268 (1995) pp. 845-847. In this case, the electrode and carbon nanotube must not make contact.

[0031] Carbon nanotubes can be directly grown on a substrate even in thermal decomposition using seeding catalysts, but the substrate temperature is high, the orientation of the carbon nanotubes that are grown cannot be controlled, and the thickness cannot be controlled either. Amorphous carbon readily grows on the tube peripheral walls. Furthermore, the junction between the substrate and carbon nanotubes is weak.

[0032] Furthermore, arc discharge requires great current and the temperature of the section of carbon nanotube growth must be extremely high. Finally, direct growth of carbon nanotubes on substrates such as quartz or metal has been impossible.

[0033] Similarly, carbon nanotubes are grown in a high-temperature frame in laser vapor deposition as well. but they can merely accumulate in the low-temperature downstream section. Consequently, their growth on a specific substrate has not been possible.

[0034] Furthermore, there has been no technique of controlling the amount of current flowing through carbon nanotubes using a magnetic field.

[0035] The growth of nanotubes in a specific orientation on a specific substrate has been extremely difficult, as clarified in aforementioned conventional techniques, and growth while one or both ends of a carbon nanotube are joined to an electrode has been impossible.

[0036] The purpose of the present invention is to resolve aforementioned problems.

[0037] Specifically, the purpose of the present invention is to provide a device in which one or both ends of a carbon nanotube are joined to an electrode on a substrate so that current can be efficiently circulated through a carbon nanotube.

[0038] Another purpose of the present invention is to provide a device capable of controlling the amount of current flowing through a carbon nanotube on a substrate via a magnetic field.

[0039] Another purpose of the present invention is to provide a method of producing a device capable of controlling the amount of current flowing through a carbon nanotube on a substrate via a magnetic field.

[0040] Furthermore, another purpose of the present invention is to provide a method of producing in which carbon nanotubes with a specific orientation on a substrate are grown.

[0041]
[Means of Solving the Problems] Aforementioned problems can be resolved by the device and production method pursuant to the present invention presented below. Specifically, the device pursuant to the present invention uses carbon nanotubes in which at least one end of said carbon nanotubes is connected to a substrate, and catalyst hyperfine particles containing one or more metals selected from Fe, Co or Ni are dispersed at the junction in material consisting essentially of one or more metals selected from Cu, Ag, Au or Cr.

[0042] The method of producing carbon nanotube devices pursuant to the present invention is one in which carbon nanotubes are grown by thermal decomposition using a catalyst on a substrate, wherein carbon nanotubes are grown from the surface of a substrate comprising catalyst hyperfine particles containing one or more metals selected from Fe, Co or Ni that are dispersed in material consisting essentially of one or more metals selected from Cu, Ag, Au or Cr, at which time the substrate with said section of dispersed catalyst hyperfine particles is heated in an atmosphere of ethylene, acetylene, gaseous carbon monoxide or a mixture thereof as a gaseous raw material at a temperature range of 400 to 800•C to bring about a thermal decomposition reaction of said gaseous raw material.

[0043] The current flowing through carbon nanotubes in the carbon nanotube device pursuant to the present invention can be controlled by an external magnetic field.

[0044]
[Mode of Implementing Invention] The preferred mode of implementing the present invention is explained below.

[0045] The substrate in the device pursuant to the present invention is Si and the catalyst hyperfine particles are metals containing one or more metals selected from Fe, Co or Ni. A carbon nanotube device in which said catalyst hyperfine particles are dispersed in material consisting essentially of Cu is especially desirable. For metals containing Fe, Co to serve as catalyst hyperfine particles and for such catalyst hyperfine particles to be dispersed in film consisting essentially of copper even when using a Si substrate are desirable for low-temperature growth of carbon nanotubes, for controlling the current by magnetic field, and for dispersion in copper.

[0046] Furthermore, carbon nanotubes are grown from the surface of a Si substrate in which catalyst hyperfine particles containing Fe or Co are dispersed in material consisting essentially of copper in a desirable mode of implementing the method of producing a device using carbon nanotubes. At that time, heating said substrate at a temperature range of 400•C to 800•C in an atmosphere containing ethylene, acetylene or carbon monoxide or a mixture thereof as a gaseous raw material to bring about thermal decomposition of the gaseous raw material would be desirable in terms of carbon-nanotube characteristics and in terms of dispersion of catalyst hyperfine particles. Of course, cyclohexane or benzene, compounds that are initially liquid but which may be evaporated to serve as gaseous raw materials may be used in addition to these gases, but ethylene, acetylene, carbon monoxide are desirable from the perspective of low-temperature growth.

[0047] It would be desirable for the diameter range of the catalyst hyperfine particles in the present invention to be several nm to several hundred nm.

[0048] Since fine-particle-dispersed GMR film is used in the explanation of the effect of the present invention, this fine-particle-dispersed GMR film is explained first.

[0049] GMR is an abbreviation of Giant Magnetic Resistance. It is a phenomenon in which the electrical resistivity of a film having a specific structure falls upon application of a magnetic field. A thin laminated metal film is commonly used, but combinations of Fe/Cr or Co/Cu and the like would be effective. Such a GMR effect is seen not only in thin laminated metal film but in hyperfine dispersed particle film (granular alloy film) as well. The cause of such a GMR effect is believed to be that the magnetic moments of fine particles and of thin laminated metal film of Fe or Co become parallel due to an external magnetic field, which thereby decreases disturbance that is dependent on the spin of conducting electrons.

[0050] Aforementioned hyperfine particle film can be produced by the concurrent sputtering method or the ICB (ionized cluster beam) method. The diameter of fine particles of Fe or Co dispersed in copper can be controlled to a certain extent by annealing after film formation or by substrate heating during film formation, and the diameter of fine particles reaches several nm to several 10 nm. Hyperfine particles of Fe, Co, etc., also are found on the surface of film obtained in aforementioned manner in which hyperfine particles are dispersed, and they can be used as growth nuclei for carbon nanotube growth.

[0051] Heat treatment of a substrate in gaseous raw material or in a gas atmosphere containing diluent gas or growth-promotion gas would be effective in growing carbon nanotubes on a substrate having such growth nuclei of catalyst hyperfine particles. Many of aforementioned gases that contain carbon can be used as gaseous raw material. Examples include gases consisting only of carbon and hydrogen such as methane, ethane, propane, butane, pentane, hexane, ethylene, acetylene, benzene, toluene, cyclohexane, or gases containing other elements such as benzonitrile, acetone, ethyl alcohol, methyl alcohol, carbon monoxide. Raw materials comprising carbon, hydrogen as well as oxygen are preferable in that they are more resistant to the inclusion of impurities although they vary somewhat based on the growth temperature, pressure, or composition, such as the type of substrate or growth nucleus. Furthermore, ethylene, acetylene, carbon monoxide are desirable when the low temperature of carbon nanotubes is considered. Hydrogen has been cited as a growth promotion gas, but it is not essential since the efficacy of hydrogen is dependent on the gaseous raw material, reaction temperature, and the composition of the growth nucleus and the like. Furthermore, diluent gases are effective when growth is too fast or if the toxicity or explosiveness are to be moderated. Inert gases such as argon or helium as well as nitrogen would be good diluent gases.

[0052] Figure 2, 4 show examples of the production process of carbon nanotube devices obtained in this manner. Figure 2 is a simplified cross-sectional view for explaining the process. Reference number 20 in Figure 2 denotes a substrate, 21 denotes pre-annealed hyperfine particle-dispersed film, 22 denotes post-annealed hyperfine particle-dispersed film, 23 denotes catalyst hyperfine particles, 24 denotes hyperfine particle-supporting film whose main element is Cu, etc., and 25 denotes carbon nanotubes. This diagram explains the concept of carbon nanotube production as follows. First, a thin film consisting essentially of Cu, Ag, Au, Cr in which metal hyperfine particles consisting essentially of Fe, Co or Ni are uniformly dispersed is produced on a substrate as shown in Figure 2a). The concurrent sputtering of two elements on a target of Cu or Co, for example, would be one method of film growth. The homogeneity of dispersion is destroyed by annealing at a temperature of 400 to 800•C in a reducing atmosphere following film growth so as to obtain hyperfine particle-dispersed film 22 in which catalyst hyperfine particles 23 such as Co, etc., are deposited within or on the surface of hyperfine particle-supporting film 24 whose main element is Cu, etc. This dispersion state is not complete since Cu forms a somewhat solid solution in catalyst hyperfine particles or, conversely, since Fe or Co form a somewhat solid solution in Cu film which is a hyperfine particle-supporting film.

[0053] Next, carbon nanotubes are grown in a reaction device as shown in Figure 4. This is explained using Figure 4, a general view of the device. Reference number 41 in Figure 4 denotes a reaction vessel, 42 denotes a substrate, and 43 denotes an infrared absorbing plate that functions as a substrate holder. Reference number 44 denotes an induction tube for gaseous raw material such as ethylene. This tube should be disposed so that the concentration of gaseous raw material near the substrate becomes uniform. Reference number 45 denotes an induction tube for reaction promoting gases such as hydrogen or for diluent gases such as helium. Reference number 49 denotes an infrared permeation window that serves to prevent clouding due to decomposition of gaseous raw materials. Reference number 46 denotes a gas exhaust line that is connected to a turbo molecular pump or a rotary pump. Reference number 47 denotes an infrared lamp used in substrate heating while reference number 48 denotes a focusing mirror for efficiently focusing infrared light on an infrared absorption plate. While omitted from the diagram, vacuum gauges to monitor the pressure within the vessel or thermocouples to measure the substrate temperature are incorporated as well. An electric oven type of device that heats the entire unit from without in addition to the device explained here is also permissible. In actual growth of carbon nanotubes, 10 sccm of the gaseous raw material ethylene would be inducted through induction tube 44, 10 sccm of hydrogen would be inducted from induction tube 45, the pressure within the vessel would be set at 1000 Pa, the substrate would be set at 700•C using an infrared lamp, and a reaction would be carried out for 60 minutes.

[0054] The resulting product is shown in Figure 2c). The diameter of the carbon nanotubes that is dependent on the diameter of catalyst hyperfine particles or on other reaction conditions ranges from several nm to the submicron diameter while the length ranges from several 10 nm to several 10 μm. Furthermore, since one or both ends of the tubes are already joined to the substrate, they are especially suited for applications including electrolytic electron discharge, pins such as STM, quantum devices, micromachine vibrators, or various types of electrodes. This is also useful as a method of improving the substrate surface since carbon is chemically stable and strong.

[0055]
[Working Example] A working example of the present invention is explained in detail below with reference to the appended figures, but the present invention is not restricted to this. It may be appropriately modified within the range of the present invention.

[0056] The carbon nanotube device and its production method pursuant to the present invention are explained using Figure 3, a simple cutaway drawing for explaining the process, and Figure 4, a general view of the device.

[0057] Reference number 41 in Figure 4 denotes a reaction vessel, 42 denotes a substrate, 43 denotes an infrared absorbent made of graphite that serves as a substrate holder. Reference number 44 denotes an induction tube of gaseous raw material that is disposed so that the concentration of gaseous raw material near the substrate becomes uniform. Reference number 45 denotes an induction tube for hydrogen gas with infrared permeation window 49 disposed near the window to prevent clouding due to decomposition of gaseous raw materials. Reference number 46 denotes an gas exhaust line that is connected to a turbo molecular pump or a rotary pump. Reference number 47 denotes an infrared lamp for heating the substrate. Reference number 48 denotes a focusing mirror to efficiently focus infrared rays onto infrared absorbing plate. Vacuum gauges to monitor the pressure within the vessel or thermocouples to measure the substrate temperature are incorporated as well.

[0058] The substrate preparations preceding carbon nanotube growth are explained first.

[0059] Initially, an electrode is created on a substrate. First, 100 nm of Co film is grown as a substrate by RF sputtering using a Si wafer substrate and a cleaned sapphire substrate. The sputtering conditions are 400 W RF power and Ar = 5 m Torr atmosphere. Next, to produce hyperfine particle-dispersed film on part of the electrode that was produced, Cu and Co, Cr and Fe, Ag and Ni, Au and Co and Ni were concurrently sputtered under conditions similar to the electrode film growth conditions after the remainder of the electrode had been covered by a metal mask, or about 200 nm of film was grown by concurrent resistance heating. The ratio of A (Cu, Cr, Ag, Au):B (Fe, Co, Ni) was set at 5:1. When this substrate was set in a reaction device as shown in Figure 4 and annealed for 20 minutes at 600•C in an atmosphere of 4% hydrogen and 96% helium, hyperfine particle-dispersed film 32 with catalyst hyperfine particles 33 of Fe, Co or Ni having particle diameter of several to several 10 nm dispersed at a high density on the surface of or within hyperfine particle-supporting film 34 of Cu, Cr, Ag, or Au then formed on the substrate surface.

[0060] Next, 10 sccm of hydrogen gas was inducted from induction tube 45 and the pressure within the reaction vessel was set at 500 Pa while the substrate with such catalyst hyperfine particles was set in the same reaction device. An infrared lamp was lit and the substrate temperature was set at 400 to 800•C. After the temperature had been stabilized, about 10 sccm of gaseous raw material such as methane, ethylene, acetylene, carbon monoxide, benzene was inducted via induction tube 44 to set the pressure within the reaction vessel at 1000 Pa, and this was maintained for 20 minutes. The infrared lamp was turned off and the gas feed was discontinued, after which the substrate temperature was returned to room temperature and the substrate was extracted to the air.

[0061] Observation of the surface of the extracted substrate with FE-SEM (Field Emission-Scanning Electron Microscope) revealed that carbon nanotubes had grown only on the hyperfine particle-dispersed film as shown in Figure 3d) in all substrates. The diameter of carbon nanotubes ranged from several nm to several 10 nm, dependent on the gaseous raw material or catalyst hyperfine particles, and the nanotubes grew vertically a certain amount from the substrate while one or both sides of the tubes are joined to the substrate. However, the growth of carbon nanotubes was reduced when methane is the source gas. Furthermore, the diameter of carbon nanotubes varied when the source gas was benzene, and the thickest ones reached several 100 nm. The ideal growth temperature for carbon nanotubes rose in sequence of carbon monoxide, acetylene, ethylene, benzene, methane. Furthermore, the most growth of carbon nanotubes was reached when catalyst hyperfine particles were dispersed in Cu on a Si wafer substrate.

[0062] To evaluate the characteristics of the resulting carbon nanotube device, it was set in a vacuum chamber after an electrode was attached to an electrode film of the substrate, and an opposing electrode was set parallel to the substrate at a position 0.1 mm apart from the substrate. Positive voltage was applied to the opposing electrodes after the chamber interior was evacuated to 10^{-6} Torr and the amount of electron discharge from the carbon nanotubes was then measured. The result revealed the amount of current to be one order of magnitude greater than that from a film in which carbon nanotubes were merely dispersed. This is believed to represent an effect of carbon nanotubes having adequate junction with the electrodes. Furthermore, the electron discharge was enhanced by 10% when a magnetic field of 1000 (Oe) was applied parallel to the film of this device. The cause is believed to be alignment by the magnetic field of the spin of the hyperfine particles of Fe, Co, Ni, etc., that are joined to carbon nanotubes. A change in the current attributable to a magnetic field was not observed in films in which carbon nanotubes were merely dispersed on electrodes. The device pursuant to the present invention was thus confirmed to actively respond due to a magnetic field.

[0063] Working Example 2 The structure and production method of a horizontal type of carbon nanotube device are explained using Figure 5, a general view and Figure 4, a general view of the device. In Figure 5, a) is a planar schematic illustration from above and b) is a transverse schematic illustration.

[0064] First, Co/Cu dispersion film 200 nm thick was grown using a metal mask on substrate 50 by the RF concurrent sputtering method similarly to Working Example 1. The sputtering conditions at this time were 400 W RF power, Ar = 5m Torr atmosphere, and the Co:Cu constituent ratio was 1:4. When this substrate was set in a reaction device as shown in Figure 4 and annealed for 20 minutes at 450•C in a vacuum at 10^{-7} Torr, Co precipitated in the dispersed film, a state of quite high-density dispersion of Co hyperfine particles of several nm to several 10 nm particle diameter was reached, and that resulted in catalyst hyperfine particle-dispersed film 53. Next, the substrate having such a catalyst hyperfine particle-dispersed film was set in the same reaction device, 20 sccm of hydrogen gas was inducted from induction tube 45, and the pressure within the reaction vessel was set at 500 Pa. An infrared lamp was lit and the substrate temperature was raised to 600•C. After the temperature was stabilized, 20 sccm of mixed gaseous raw material comprising acetylene that was diluted to 10% by nitrogen was inducted, and this was held for 20 minutes while the pressure within the reaction vessel was at 1000 Pa. Acetylene was set so as to flow from substrate A to B here. The infrared lamp was turned off and the gas feed was discontinued, after which the substrate temperature was returned to room temperature and the substrate was extracted to the air. Next, 100 nm only of film was grown on Co electrodes 51, 52 by sputtering after covering by a metal mask. At this time, the majority of the tips of carbon nanotubes 54 were covered by electrode 52 and were electrically connected.

[0065] Observation of the surface of the resulting substrate by Fe-SEM revealed growth of carbon nanotubes 54 from catalyst hyperfine particle-dispersed film 53 in the direction from A to B along the flow of source gas, and electrodes 51, 52 were joined by carbon nanotubes, as shown in Figure 5a, b). The diameter of carbon nanotubes 54 was several nm to several 10 nm.

[0066] To evaluate the characteristics of the resulting carbon nanotube device, electrodes 51, 52 of the substrate were wired, followed by application of voltage and magnetic field, and the current - voltage characteristics were measured. The magnetic field at this time was applied perpendicular to A-B in Figure 5. When a given voltage was applied, current about 10% greater than the initial level without a magnetic field was observed at 1 tesla, and it remained about 3% greater than the initial current level without a magnetic field even when the magnetic field was returned to zero in that state. This confirmed that the device pursuant to the present invention could perceive hysteresis of a magnetic field. Furthermore, no response to a magnetic field was seen in a device with platinum electrodes produced from above and with carbon nanotubes dispersed on a substrate for comparison.

[0067] Working Example 3 The structure and production method of a Tip type of carbon nanotube device are explained using Figure 6, a simplified cross-sectional view and Figure 4, a general view of the device.

[0068] An Si wafer that constitutes substrate 60 was formed in girder shape as shown in Figure 6 a) by photolithography, after which a Co electrode 61 film 100 nm thick was grown thereupon by sputtering. Hyperfine particle-dispersed section 62 was then produced on part of the girder. Film with a minute orifice was mounted on electrode 61 in the production of hyperfine particle-dispersed section 62. Co and Cu were slant deposited by resistance heating, followed by removal of the orifice. The ratio of Co to Cu at this time was about 1:4. When this substrate was set in a reaction device as shown in Figure 4 and annealed for 20 minutes at 450•C in a vacuum at 10^{-7} Torr, Co precipitated in the dispersed film, a state of quite high-density dispersion of Co catalyst hyperfine particles 63 of several nm to several 10 nm particle diameter was reached. Next, the substrate having such a catalyst hyperfine particle-dispersed film was set in the same reaction device, 20 sccm of hydrogen gas was inducted from induction tube 45, and the pressure within the reaction vessel was set at 500 Pa. An infrared lamp was lit and the substrate temperature was raised to 700•C. After the temperature was stabilized, 20 sccm of ethylene gas was inducted, and this was held for 20 minutes while the pressure within the reaction vessel was at 1000 Pa. The infrared lamp was turned off and the gas feed was discontinued, after which the substrate temperature was returned to room temperature and the substrate was extracted to the air.

[0069] Observation of the surface of the resulting substrate by Fe-SEM revealed growth of carbon nanotubes from catalyst hyperfine particles 63 on the surface of hyperfine particle-dispersed section 62, as shown in Figure 6c. The diameter of the carbon nanotubes was several nm to several 10 nm.

[0070] To evaluate the characteristics of the resulting carbon nanotube device, the substrate was attached to STM, AFM evaluation devices and electrode 61 was also wired at that time. The results of STM, AFM evaluation revealed good images due to the carbon nanotube Tip. The domain structure of the magnetized film was also observed by STM. This is concluded to be an effect of connecting carbon nanotubes to film having the GMR effect.

[0071]
[Effects of Invention] The following effects can be attained by using the carbon nanotube production method explained above.

[0072] 1) A carbon nanotube device having good electrical contact with electrodes can be provided.

[0073] 2) A carbon nanotube device in which the current can be controlled by a magnetic field can be provided.

[0074] 3) Carbon nanotubes joined at one or both ends to electrodes can be grown.

[0075] 4) Carbon nanotubes which are uniform to a certain degree in both diameter and orientation can be created.

[0076] 5) Carbon nanotubes can be grown directly at any position on a substrate.

Explanation of Diagrams
[Brief Description of Drawings]

[Figure 1] A simplified diagram showing the structure of carbon wires. a) shows an isotropic carbon fiber, b) shows a carbon nanotube with amorphous carbon adhering about the periphery, c) shows a multi-wall (carbon) nanotube, d) shows a single wall (carbon) nanotube.

[Figure 2] A simplified cross-sectional view for explaining the production process of a longitudinal type of carbon nanotube device. a) shows film growth of a hyperfine particle-dispersed film (pre-annealed) on a substrate, b) shows the state of the film after annealing, c) shows the state of the device after carbon-nanotube growth.

[Figure 3] A simplified cross-sectional view for explaining the production process of the carbon nanotube device of working example 1. a) shows film growth of an electrode film on a substrate, b) shows film growth of a hyperfine particle-dispersed film (pre-annealed) thereupon, c) shows the state of the film after annealing, d) shows the state of the device after carbon-nanotube growth.

[Figure 4] General view of a device for carbon nanotube growth.

[Figure 5] A simplified diagram for explaining the structure of a transverse type of carbon nanotube device. a) is a planar view from above, b) is a transverse section.

[Figure 6] A simplified cross-sectional view for explaining the production process of a Tip type of carbon nanotube device. a) shows film growth of an electrode film on a substrate, b) shows the state of installation of a hyperfine particle-dispersed section on part thereof, c) shows the state of the device following growth of carbon nanotubes on the surface of that section.

[Explanation of Symbols]

20 substrate
21 hyperfine particle-dispersed film (pre-annealed)
22 hyperfine particle-dispersed film (post-annealed)
23 catalyst hyperfine particles

24 hyperfine particle-supporting film
25 carbon nanotube
30 substrate
31 electrode film
32 hyperfine particle-dispersed film
33 catalyst hyperfine particles
34 hyperfine particle-supporting film
35 carbon nanotube
41 reaction vessel
42 substrate
43 infrared absorbing plate
44 gaseous raw material induction tube
45 growth promotion and diluent gas induction tube
46 exhaust line
47 infrared lamp
48 infrared focusing mirror
49 infrared permeation window
50 substrate
51 electrode
52 electrode
53 catalyst hyperfine particle-dispersed film
54 carbon nanotube
60 substrate
61 electrode
62 hyperfine particle-dispersed section
63 catalyst hyperfine particles
64 carbon nanotube

Figure 1

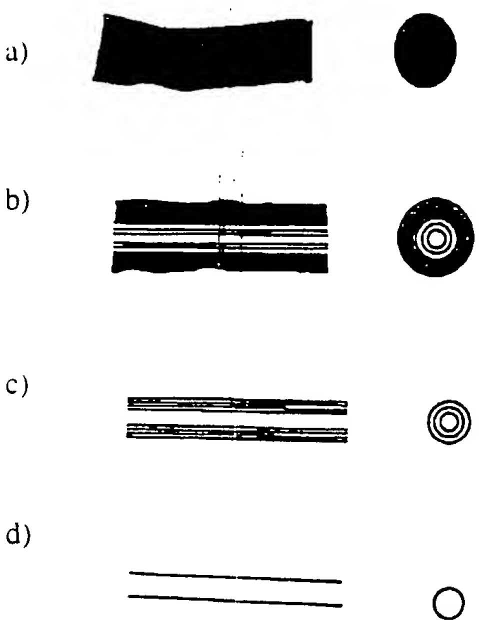
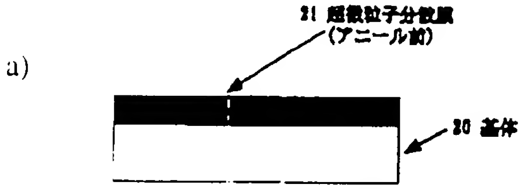
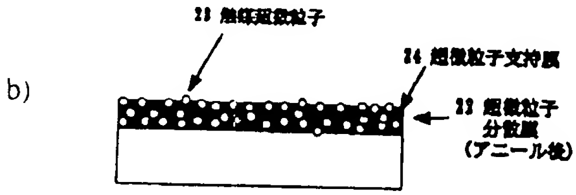


Figure 2

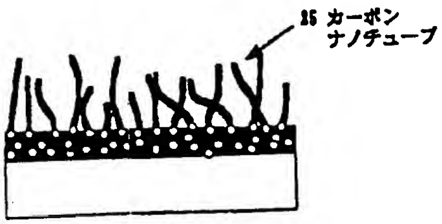

a)
21 超微粒子分散膜
(アニール前)
20 基体

21 hyperfine particle-dispersed film (pre-annealed)
20 substrate


b)
23 触媒超微粒子
24 超微粒子支持膜
22 超微粒子
分散膜
(アニール後)

23 catalyst hyperfine particles
24 hyperfine particle-supporting film
22 hyperfine particle-dispersed film (post-annealed)

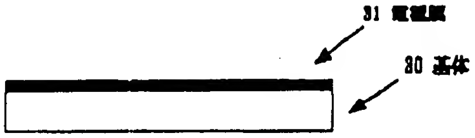
c)


25 カーボン
ナノチューブ

25 carbon nanotube

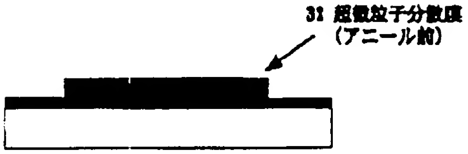
Figure 3

a)



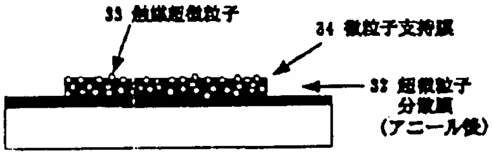
31 electrode film
30 substrate

b)

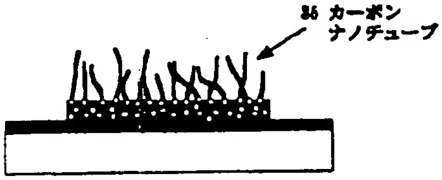

32 超微粒子分散膜
(アニール前)

32 hyperfine particle-dispersed film (pre-annealed)

c)


33 触媒超微粒子
34 微粒子支持膜
32 超微粒子
分散膜
(アニール後)

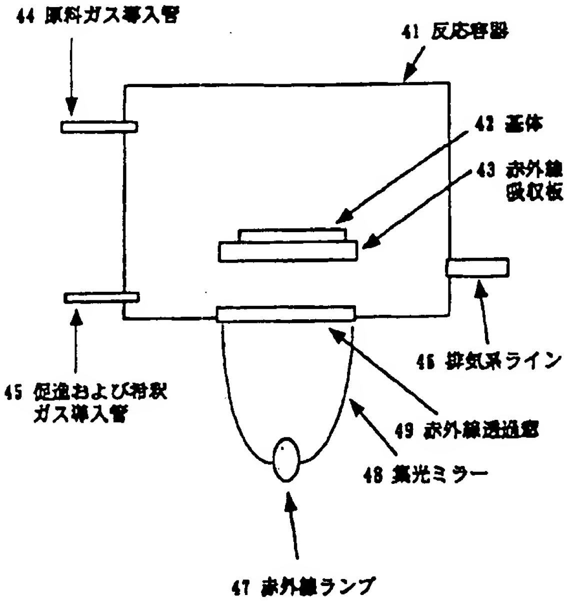
33 catalyst hyperfine particles
34 hyperfine particle-supporting film
32 hyperfine particle-dispersed film (post-annealed)


35 カーボン
ナノチューブ

d)

35 carbon nanotube

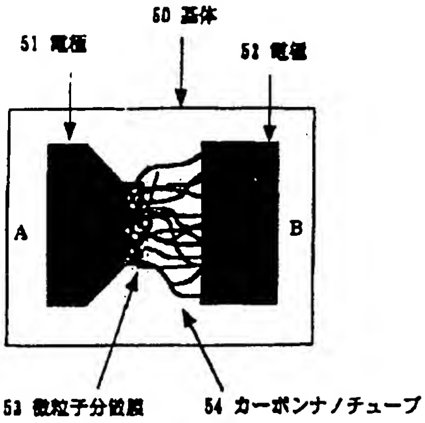
Figure 4


44 原料ガス導入管
41 反応容器
42 基体
43 赤外線
吸収板
46 排気系ライン
45 促進および希釈
ガス導入管
49 赤外線透過窓
48 集光ミラー
47 赤外線ランプ

41 reaction vessel
42 substrate
43 infrared absorbing plate
44 gaseous raw material induction tube
45 growth promotion and diluent gas induction tube
46 exhaust line
47 infrared lamp
48 focusing mirror
49 infrared permeation window

Figure 5

a)


50 基体
51 電極
52 電極
A
B
53 微粒子分散膜
54 カーボンナノチューブ

50 substrate
51 electrode
52 electrode
53 catalyst hyperfine particle-dispersed film
54 carbon nanotube

b)

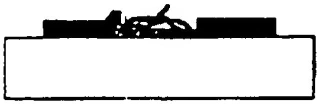
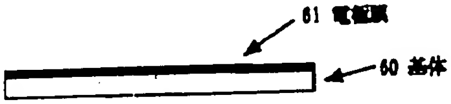


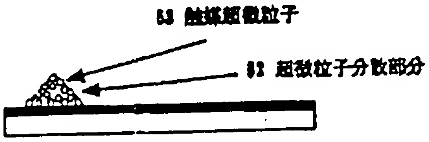
Figure 6

a)



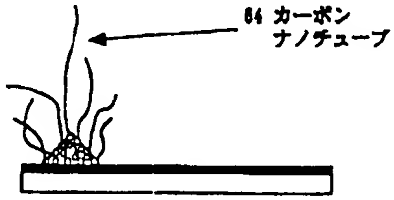
61 electrode
60 substrate

b)


63 触媒超微粒子
62 超微粒子分散部分

63 catalyst hyperfine particles
62 hyperfine particle-dispersed section

c)


64 カーボン
ナノチューブ

64 carbon nanotube